

Thermoelectric performance of granular semiconductors

Andreas Glatz¹ and I. S. Beloborodov²

¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

²Department of Physics and Astronomy, California State University Northridge, Northridge, CA 91330, USA

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We study thermoelectric properties of granular semiconductors with weak tunneling conductance between the grains, $g_t < 1$. We calculate the thermopower and figure of merit taking into account the shift of the chemical potential and the asymmetry of the density of states in the vicinity of the Fermi surface due to n- or p-type doping in the Efros-Shklovskii regime for temperatures less than the charging energy. We show that for weakly coupled semiconducting grains the figure of merit is optimized for grain sizes of order 5nm for typical materials and its values can be larger than one. We also study the case of compensated granular semiconductors and show that in this case the thermopower can be still finite, although two to three orders of magnitude smaller than in the uncompensated regime.

A major research area in nano-science and materials physics is the search for highly efficient thermoelectric materials. Although there has been extensive research efforts in the last several decades, the progress in this quest has been limited until recently. It was found that for further improvement in efficiency *inhomogeneous/granular* thermoelectric semiconductors are especially suited [1]. These materials are now accessible as next generation devices for conversion of thermal to electrical energy and vice versa and technologically important due to the possibility of direct control of the system parameters. The dimensionless *figure of merit*, $ZT = S^2\sigma T/\kappa$, is the preferred measure for the performance or efficiency of thermoelectric materials, where S is the thermopower and σ and κ the electric and thermal conductivities, respectively [2, 3]. Recently, ZT values of 2.4 in layered nanoscale structures [4] at 300K, and 3.2 for a bulk semiconductors with nanoscale inclusions [5] at about 600K were reported. These high values of ZT are in the range for applications and therefore call for the development of a comprehensive quantitative description of thermoelectric properties of granular semiconductors, which can serve as basis for a new generation of thermoelectrics.

In this paper we investigate the thermopower S and the figure of merit ZT of granular semiconductors focusing on the case of weak coupling between the grains, $g_t < 1$, see Fig. 1. Each semiconducting nanocrystal is characterized by two energy scales: (i) the mean energy level spacing $\delta = 1/(na^d)$, where n is the density of states at the Fermi surface, a is the grain size, and d is the dimensionality of a grain, and (ii) the charging energy $E_c = e^2/(\epsilon_r a)$ with ϵ_r being the dielectric constant. In semiconductors the density of states n is of about two orders of magnitude smaller than that in metals. Thus in semiconducting dots δ can be of order of the charging energy, $\delta \sim E_c$, in contrast to metallic granular materials where typically $\delta \ll E_c$ [6]. Our considerations are valid for temperatures $T < E_c$.

The internal conductance of a grain is taken larger than the inter-grain tunneling conductance, g_t , which controls

macroscopic transport properties of the sample [7]. In this paper we consider $g_t < 1$, i.e., smaller than the quantum conductance, which is the typical experimental situation [4, 5].

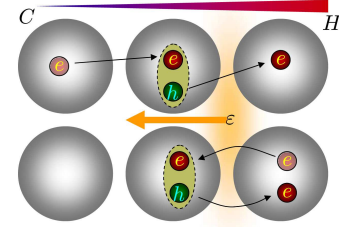


FIG. 1: (Color online) Sketch of a nanogranular material showing typical electron (e) and hole (h) transport. In the upper row of grains an inelastic electron tunneling process is shown and in the lower row a co-tunneling loop responsible for the electronic part of the heat transport is presented. The energy (ϵ) transport goes from the "hot" (H) to the "cold" (C) side.

In the case of diagonal (short range) Coulomb interaction, the total probability for an electron tunneling through many grains via elastic or inelastic co-tunneling can be written as the product, $P = \prod_{i=1}^N P_i$, of the individual probabilities of single elastic/inelastic co-tunneling events through single grains with $N = r/a$ is the number of grains. The probability P is related to the localization length ξ as $P \sim e^{-r/\xi}$.

Semiconducting nanocrystal arrays are described by the Hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}^{(i)} + \sum_{\langle ij \rangle, k_i, k_j} \left[t_{ij} \hat{c}_{k_i}^{(i)\dagger} \hat{c}_{k_j}^{(j)} + \text{h.c.} \right], \quad (1)$$

where i, j are the grain indexes and the summation in the second term of the r.h.s. of Eq. (1) is performed over nearest neighbors. The term $\mathcal{H}^{(i)}$ is the Hamiltonian for the single grain i including the free electron energy and the diagonal Coulomb interaction, and the second term is the tunneling Hamiltonian between the adjacent grains

i and j with t_{ij} being random tunneling matrix elements and $\hat{c}_{k_i}^{(i)\dagger}$ [$\hat{c}_{k_i}^{(i)}$] the creation [annihilation] operator on the i th grain. Due to the large mean energy level spacing in semiconducting grains $\delta \sim E_c$, only a few terms of the k -sums are important.

In Ref. [8] it was shown that the probability for elastic P_i^{el} and inelastic P_i^{in} co-tunneling through an array of weakly coupled semiconducting grains has the form

$$P_i^{el} = \frac{1}{[\tau \max(\delta, E_c)]^2}, \quad P_i^{in} = \frac{e^{-2\delta/T}}{[\tau \max(\delta, E_c)]^2}, \quad (2)$$

where τ is the electron escape time from a grain. Thus, for the elastic/inelastic localization length we obtain

$$\xi^{el} \sim \frac{a/2}{\ln[\tau \max(\delta, E_c)]}, \quad \xi^{in} \sim \frac{a/2}{\ln[\tau \max(\delta, E_c)] + \delta/T}. \quad (3)$$

The localization length $\xi^{el/in}$ is related to the characteristic temperature scale $T_0 = e^2/(\epsilon_r \xi^{el/in})$, which is of order $E_c \ln P_i^{-1}$. Below we derive the thermopower, S , thermal conductivity, κ , and figure of merit, ZT for granular semiconductors using Eq. (3).

One remark is in order: The thermopower S of lightly doped compensated semiconductors was investigated in the past [9, 10, 11, 12]. However, all previous studies were concentrated on the Mott variable range hopping (VRH) regime, with conductivity being $\sigma(T) \sim \exp(T_M/T)^{1/4}$, where T_M is the Mott temperature [13]. In granular materials the Mott VRH regime is hard to observe. Indeed, in semiconductors the Efros-Shklovskii (ES) law [14, 15]

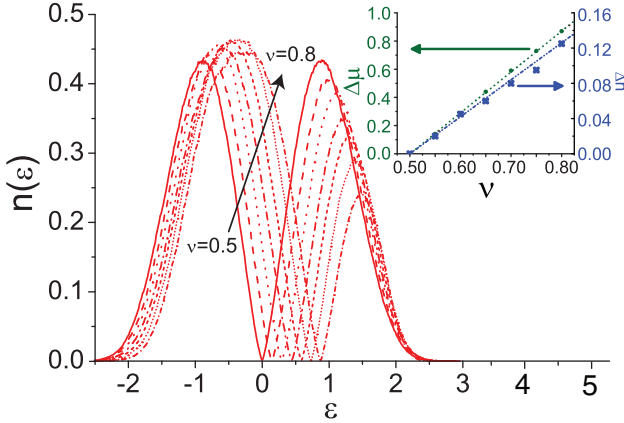


FIG. 2: (Color online) Simulation results for the density of state $n(\varepsilon)$ vs. energy ε for different filling factors ν , indicated by the arrow across the curves from $\nu = 0.5$ to $\nu = 0.8$ in steps of $\Delta\nu = 0.05$ ($\nu > 1/2$ corresponds to n-type doped semiconductors). The simulations were done for a 2D Coulomb glass model, simulating the whole weakly coupled granular sample [16, 17] for a system size of 500^2 . The inset shows the dependence of the shift of the chemical potential $\Delta\mu$ and the asymmetry of the density of states Δn on ν (see text). Using these data we extract the numerical coefficients $a_1 \approx 2.9$ and $a_2 \approx 0.4$ in Eq. (7) by linear fitting.

may turn into the Mott behavior with an increase of temperature. This happens when the typical electron energy ε involved in a hopping process becomes larger than the width of the Coulomb gap Δ_c , i.e. when it falls into the flat region of the density of states where Mott behavior is expected. To estimate the width of the Coulomb gap Δ_c , one compares the ES expression for the density of states $n(\Delta_c) \sim (\epsilon_r/e^2)^d |\Delta_c|^{d-1}$ with the DOS in the absence of the long-range part of the Coulomb interaction, n_0 ($d = 2, 3$ is the dimensionality of a sample). Using the condition $n(\Delta_c) \sim n_0$ we obtain $\Delta_c = (n_0 e^{2d}/\epsilon_r^d)^{\frac{1}{d-1}}$. Inserting the value for the bare DOS, $n_0 = 1/E_c \xi^d$, into the last expression we finally obtain $\Delta_c \sim E_c$. This means that there is no flat region in the DOS for $T < E_c$.

Here we discuss two effects: i) we calculate the thermopower S of granular semiconductors taking into account the shift of the chemical potential $\Delta\mu = a_1(\nu - 1/2)T_0$ with ν being the electron filling factor (ν is related to the compensation level of semiconductors, here we concentrate on n-type doped semiconductors with $1/2 < |\nu| < 1$), a_1 a dimensionless numerical coefficient, and the asymmetry of the density of states (DOS) $\Delta n = a_2(\nu - 1/2)T_0^{-1}$ with a_2 being a numerical constant; ii) we show that even in the absence of the chemical potential shift, $\Delta\mu = 0$, and asymmetry of DOS, $\Delta n = 0$, the thermopower S is still finite, although small, due to co-tunneling processes. We start with the former case.

To calculate the thermopower of granular materials in the regime of weak coupling between the grains it is necessary to take into account electrons and holes because the contributions of electrons and holes cancel in the leading order. In general the thermopower is proportional to the average energy transferred by charge carriers and can be written as [9, 10, 11, 12]

$$S = -\frac{1}{2eT} [\langle \varepsilon - \tilde{\mu} \rangle_e + \langle \varepsilon - \tilde{\mu} \rangle_h]. \quad (4)$$

Here the subscripts e and h refer to electrons and holes and $\tilde{\mu} = \mu + \Delta\mu$ is the shifted chemical potential. The expression in the square brackets of the r.h.s. of Eq. (4) describes the average energy transferred by charge carriers (electron or hole) measured with respect to the shifted chemical potential $\tilde{\mu}$. The average energy in Eq. (4) can be calculated as follows

$$\langle \varepsilon - \tilde{\mu} \rangle_{e/h} = \frac{\int_0^\infty d\varepsilon (\varepsilon - \tilde{\mu}) n(\varepsilon - \tilde{\mu}) f_{e/h}(\varepsilon - \tilde{\mu}) e^{-\frac{(\varepsilon - \tilde{\mu})^2}{2\Delta^2}}}{\int_0^\infty d\varepsilon n(\varepsilon - \tilde{\mu}) f_{e/h}(\varepsilon - \tilde{\mu}) e^{-\frac{(\varepsilon - \tilde{\mu})^2}{2\Delta^2}}}. \quad (5)$$

Here $f_{e/h}(\varepsilon)$ is the Fermi function for electrons or holes, $\Delta = \sqrt{T_0 T}$ the typical transfer energy in one hop, and $n(\varepsilon)$ is energy dependent the DOS. As we will see later, it is crucial to take into account the asymmetry of the DOS and the shift of the chemical potential in order to obtain a finite result in Eq. (4).

The DOS, $n(\varepsilon)$ in Eq. (5) for $\tilde{\mu} - \Delta_c < \varepsilon < \tilde{\mu}$ has the following form [10]

$$n(\varepsilon) \propto |\varepsilon - \tilde{\mu}|^{d-1} [1 - (\varepsilon - \tilde{\mu})\Delta n], \quad (6)$$

and is constant, n_0 , outside the Coulomb gap region, $\varepsilon < \tilde{\mu} - \Delta_c$ and $\varepsilon > \tilde{\mu}$, where $\Delta_c \sim E_c$ is the width of the Coulomb gap. The shift of the chemical potential $\Delta\mu = \tilde{\mu} - \mu$ and the asymmetry of the DOS, Δn , are explicitly defined above Eq. (4).

To support our choice for the expression of the DOS $n(\varepsilon)$ in Eq. (6) we numerically compute the DOS for a 2D Coulomb glass model to simulate the whole system of semiconducting grains (see Refs. [16, 17] for details) at arbitrary filling factor ν using first principles. The result of the simulations is shown in Fig. 2. These simulations clearly indicate that for a filling factor $\nu \neq 1/2$, the DOS is asymmetric and the chemical potential is shifted. Using these results we can identify the dimensionless numerical coefficients $a_1 \simeq 2.9$ and $a_2 \simeq 0.4$ by a simple linear fit. We note that $a_1 \gg a_2$, thus the contribution to the thermopower caused by $\Delta\mu$ in Eq. (7) is dominant.

Now, we can calculate Eq. (5) and the analog contribution for holes using Eq. (6) for the DOS together with the numerically found values for $a_{1,2}$ [20]. Finally we derive the expression for the thermopower S of granular semiconductors in the limit of weak coupling between the grains

$$S = -\frac{d[\Delta\mu + \Delta n T_0 T]}{eT} = \frac{1/2 - \nu}{e} d \left[a_1 \frac{T_0}{T} + a_2 \right]. \quad (7)$$

We note that the r.h.s. of Eq. (7) vanishes for filling factor $\nu = 1/2$, i.e., for compensated semiconductors.

Equation (7) is valid for temperatures $T < T_0 = E_c \ln P_i^{-1}$ and weak coupling between the grains $g_t < 1$. Under this condition, the electric conductivity σ is [7, 8]

$$\sigma \simeq 2e^2 a^{2-d} g_t e^{-\sqrt{T_0/T}}. \quad (8)$$

The thermal conductivity κ consists of two parts: the electron, κ_e and phonon, κ_{ph} . The phonon contribution κ_{ph} at temperatures $T \leq \Theta_D$, where Θ_D is the Debye temperature is given by [18, 19]

$$\kappa_{ph} \sim l_{ph}^{2-d} T [T/\Theta_D]^{d-1}, \quad (9)$$

where $l_{ph} = \lambda_F \exp(\Theta_D/[aT/\lambda_F])$ is the phonon mean free path in granular semiconductors with λ_F being the Fermi length. [For $a \simeq 10\text{nm}$, $\lambda_F \simeq 1\text{\AA}$, $\Theta_D \sim 450\text{K}$, one obtains $l_{ph} \simeq 1\text{nm}$ at $T \simeq 200\text{K}$] The main contribution to the electric part κ_e of the thermal conductivity κ appears due to a single closed co-tunneling loop (see Fig. 1). An electron executing a co-tunneling loop brings back its charge to the starting grain and hence there is little change in the electrical conductivity and therefore the classical activation term is absent. However, there

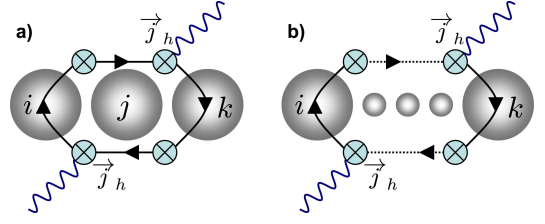


FIG. 3: (Color online) Diagrams describing lowest (a) and higher (b) order co-tunneling processes (multiple tunneling events are indicated by the dotted lines). The solid lines denote the propagator of electrons. The tunneling vertices are described by the circles. The wavy lines indicate the external coupling to the heat vertices.

is no requirement that the returning electron has exactly the same energy (due to inelastic processes). The leading contribution to κ_e is proportional to g_t^2 and is depicted in the diagram shown in Fig. 3a). The analytical result corresponding to this process can be estimated as follows

$$\kappa_e \sim g_t^2 a^{2-d} T \frac{e^{-2\delta/T}}{[\tau \max(\delta, E_c)]^2}, \quad (10)$$

where we used Eq. (2) for the inelastic co-tunneling probability P_i^{in} . Since at relatively high temperatures the phonon contribution κ_{ph} to thermal conductivity is dominant, we can neglect the contribution κ_e in the following.

Substituting Eqs. (7) and (9) into the expression for the figure of merit $ZT \simeq S^2 \sigma T / \kappa_{ph}$ we obtain the result

$$ZT \sim \frac{2d^2 g_t e^{-\sqrt{T_0/T}} [\Delta\mu/T + \Delta n T_0]^2}{(\lambda_F/a)^{2-d} (T/\Theta_D)^{d-1}} e^{(d-2) \frac{\Theta_D \lambda_F}{T a}}. \quad (11)$$

Here the expressions for $\Delta\mu$ and Δn are given above Eq. (4). Using Eq. (11) we can calculate the temperature T^* at which ZT has its maximum value, given by the solution of the quadratic equation $T^* = \frac{4}{T_0} (\alpha + (d+1)T^*)^2$, where $\alpha = (2-d)\Theta_D \lambda_F / a$. In $d = 2$ we get $T_{2D}^* = T_0/[4(d+1)]$, while in 3D the existence of a maximum depends on the values of α and T_0 .

In Fig. 4 we plotted the figure of merit ZT for a two- and three-dimensional system, using typical parameters for granular semiconductors: $\lambda_F \simeq 1\text{\AA}$, $\Theta_D \simeq 450\text{K}$, $T_0 \simeq 2E_c$, $\epsilon_r \simeq 4$, and $g_t \simeq 0.1$. Figure 4a) shows the temperature dependence of ZT for two different filling factors $\nu = 0.6, 0.65$ for a grain size of $a \simeq 5\text{nm}$ (For this size and the above dielectric constant we get $E_c \sim 800\text{K}$). We clearly see that the figure of merit can well exceed one. However, we remark that ZT depends inversely proportional on the numerical coefficient of κ_{ph} , which is assumed to be one here. Figure 4b) shows the grain size dependence of ZT at fixed temperature $T = 200\text{K}$. At this temperature for the above system parameters, the figure of merit is optimal for grain sizes $a_{3D}^* \simeq 4\text{nm}$ in 3D and $a_{2D}^* \simeq 6\text{nm}$ in 2D.

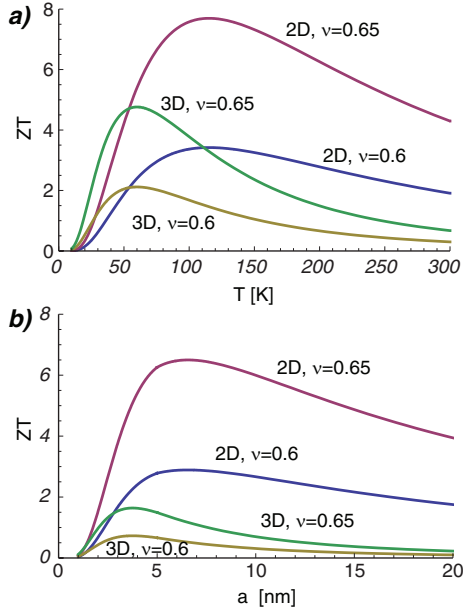


FIG. 4: (Color online) Plots of the figure of merit ZT vs temperature T (a) and grain size a (b) for two (2D) and three (3D) dimensional samples and two different filling factors $\nu = 0.6, 0.65$ (n-type doped granular semiconductors). Typical material parameters are given in the text. In a), the grain size is chosen to be $a = 5$ nm and in b), the temperature is fixed at 200 K. One sees that ZT can be optimized by choosing appropriate grain sizes: For the used parameters, these sizes are about 4 nm in 3D and 6 nm in 2D.

Now, we concentrate on the compensated regime (filling factor $\nu = 1/2$). In this case Eq. (7) predicts zero thermopower S . Thus, the fundamental question exists what mechanism may lead to a finite thermopower in this case. We start our consideration with the fact that the thermopower S can be expressed in terms of the thermoelectric coefficient η and the electric conductivity σ as $S = \eta/\sigma$. Thus, to calculate the thermopower S one has to know the thermoelectric coefficient η . To estimate $\tilde{\eta}$ we use the diagram shown in Fig. 3b) (here the tilde indicates the compensated case). Since the dominant contribution to $\tilde{\eta}$ vanishes due to particle-hole symmetry, to obtain a nonzero result it is necessary to take into account the fact that the tunneling matrix elements t and the density of states n depend on energy. In the leading order, the corrections to both quantities are proportional to T/E_F , where E_F is Fermi energy [6]. As a result, the thermoelectric coefficient is given by the expression

$$\tilde{\eta} \sim e a^{2-d} g_t [T/E_F] e^{-\sqrt{T_0/T}}, \quad (12)$$

where the temperature scale T_0 was defined below Eq. (3). Substituting Eq. (8) and (12) into the expression for thermopower we obtain

$$\tilde{S} \sim (1/e) (T/E_F). \quad (13)$$

It follows that the thermopower is finite although small,

leading to a small figure of merit as well, since $ZT \sim S^2$. Using Eqs. (7) and (13) one can see that the ratio of two thermopowers for compensated [$\nu = 1/2$, Eq. (13)] and for n-type ($\nu > 1/2$, Eq. (7)) regimes is of order $\tilde{S}/S \sim T^2/(T_0 E_F) \sim 10^{-3} - 10^{-2} \ll 1$.

In conclusion, we studied thermoelectric properties of granular semiconductors at weak tunneling conductance between the grains, $g_t < 1$. We calculated the thermopower S and figure of merit ZT taking into account the shift of the chemical potential and asymmetry of the density of states for the exemplary case of n-type doping. We showed that the weak coupling between the grains leads to a high thermopower and a low thermal conductivity resulting in relatively high values of the figure of merit. We also discussed the case of compensated (half filling, $\nu = 1/2$) granular semiconductors. We showed that in this regime the thermopower is finite, but rather small.

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